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## Certificate

Benckiser N.V. of Amsterdam/ the Netherlands filed a patent application entitled

"Composition for use in a water reservoir"

at the German Patent and Trademark Office on 29 July 1998.

The attached documents are a true and exact copy of the original documents pertaining to this patent application.

The application has provisionally been given classification C 11 D 17/00 under the International Patent Classification at the German Patent and Trademark Office.

Munich, 24 August 1999

**German Patent and Trademark Office**

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New application  
(Patent)

**BK3669**

28 July 1998

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"Composition for use in a water reservoir "

The present invention relates to a composition for use in a water reservoir, in the kitchen or in the bathroom environment.

Compositions of this type are known in various formats for different applications, for example for removing lime scale from coffee machines or for cleaning and removing lime scale from toilets as an additive placed in the water cistern.

The objective of the present invention was to find a way of simultaneously dispensing substances that are not totally compatible with one another when applied simultaneously and which release their function (s) at different, specific defined points in time.

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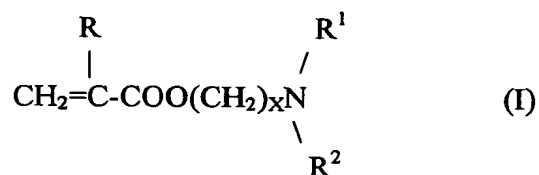
Patent specifications DE-OS 20 65 153 and DE-OS 20 07 413 disclose detergent tablets for use as washing agents, in which two components with different functions are used in combination with one another. The structure consists of a shell casing, assembled from two shell halves made from a cleansing agent and a cavity enclosed by the shells, containing additives such as softeners, brighteners, etc.

British patent 1 390 503 discloses a liquid cleansing agent or detergent containing capsules, which are insoluble in the composition, but release their contents when the composition is diluted with water. This objective is achieved by the fact that the capsules are coated with a substance, which is not readily soluble in aqueous solutions with a high ion content but is soluble when the ion content is reduced by dilution. It should be pointed out that this technique can be used as a means of incorporating materials in the liquid detergent which are intrinsically unstable in the liquid detergent or would become unstable if they were added directly. This technique is also suggested as a means of delaying the release of a specific substance.

US patent 4,082,678 describes a fabric conditioner, which comprises a closed container enclosing a releasable agent, the purpose of which is to render insoluble in water or non-dispersible in water an inner container, which is normally water-soluble or dispersible in water, disposed inside the first container, the inner container enclosing a fabric conditioner.

Japanese patent applications KOKAI 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598 describe methods of producing pH-sensitive microcapsules for use in detergents. The pH-sensitive coating is a copolymer of the following monomers:

A) at least one basic monomer of formula (I):



in which R stands for hydrogen or a methylene group, R<sup>1</sup> and R<sup>2</sup> respectively stand for an alkyl group with 1-3 carbon atoms and x is a whole number from 1 - 4;

B) at least one monomer which is insoluble or not readily soluble in water; and

C) at least one water-soluble monomer.

The described polymers are said to be insoluble at a pH value of 9.5 and higher and soluble at a pH value of 8.5 or less. Cleansing compositions containing different substances are described which can successfully and effectively be coated using the described polymers. The objective of the invention described here is to protect substances which do not release their function until the rinse cycle until the cycle starts and then to delay the release as far as possible.

A disadvantage of the solution described in these Japanese patent applications is that the encased particles are in direct contact with non-alkaline washing water at the start of the washing cycle which can cause the protective casing to start dissolving.

Japanese patent specification KOKAI 50-77406 discloses a washing detergent, which is encased in a water-soluble casing, obtained by mixing polyvinyl acetal dialkylamino acetate and at least one organic acid, which is solid at room temperature. The purpose of this protective casing is to protect the washing detergent during the main washing cycle and to release it during rinse cycles. The described compound reacts to the change in pH-value between the

main washing cycle and the rinse cycle. Here again, the disadvantage is that the protective casing could start to dissolve at the start of the washing cycle.

European patent applications EP 284 191 A2 and EP 284 334 A2 disclose a water-soluble polymer film for releasing washing additives during the rinse cycle of washing machines, which remain intact during the normal washing cycle over a range of typical temperatures and rapidly dissolve during the rinse cycle. These applications point out that the use of pH-sensitive coatings was admittedly known, but that these films are normally also temperature-sensitive, which means that they can not be relied on to remain stable at the various temperatures of the washing cycle. The proposed solution is a pH-dependent material (which undesirably also has a positive, temperature-dependent dissolving behaviour) combined with a material having a negative, temperature-dependent dissolving behaviour. This combination is supposed to guarantee that the coatings do not dissolve at the high temperatures prevailing at the start of the washing cycle (in particular the very high temperatures used in American machines).

European patent application EP 0 481 547 A1 discloses multi-layer dishwasher tablets having a core, a separating layer surrounding the core and an outer layer for the sequential release of the substances contained in the different layers. This tablet is basically intended to solve two problems, namely 1) incompatible materials can be formulated together in a single tablet and released at different times in order to avoid mutual interaction and 2) compositions, which are intended to evolve their functions at different times, can be formulated in a single tablet.

A major disadvantage of this prior art is that temperature and in particular the contact time with the washing solution is used as a means of initiating dissolution of the surrounding layer, which obviously limits the practical feasibility of the described products.

PCT application WO 95/29982 discloses a dishwasher rinsing agent in which the release of a clear rinsing agent is delayed, provided in the form of a non-ionic surfactant used with an in-

organic builder salt forming a core, which is provided with a waxy coating to ensure the delayed release. This coating is a substance which does not melt at the operating temperatures encountered during the cleaning cycle, but which chemically disintegrates so gradually at alkaline pH-values that an effective quantity of clear rinsing agent is still present at the end of the main cleaning cycle and is transferred into the rinse clear cycle.

The disadvantage of this is that the coating is rendered soluble by chemical saponification at alkaline pH-values, so that the time at which the clear rinsing substance is released from the core depends on both the temperature and the length of the main cleaning cycle. The patent application contains no teaching as to how a product is to be formulated so that the clear rinsing agent can be released in all washing programmes of any machine type during the clear rinse cycle only. Finally, the product is a mixture of granular cleaning agents and granular clear rinsing particles.

Against the background of the prior art described above, the underlying objective of the present invention is to propose a composition which enables products with different functions to be released simultaneously at different, defined times. The aim is to achieve this without significantly limiting the choice of materials which can be combined with one another.

This objective is achieved by the invention by means of a composition characterised by a basic composition which starts to function essentially when the water tank is first filled with water; and at least one particle with at least one core comprising at least one substance, which starts to function substantially after at least some of the water from the first filling process has been emptied from the water tank and fresh water is added, and a coating substantially completely encasing the core or cores and containing at least one compound, the solubility of which increases as the concentration of a specific substance in the surrounding medium decreases, and agents are provided so that the covering of the core or cores is essentially prevented from dissolving or becoming substantially detached until the inflow of fresh water.

In one advantageous embodiment, the concentration of the specific compound in the local environment of the particle or particles is high enough until the inflow of fresh water to the water reservoir to prevent the covering of the core or cores from dissolving or becoming detached to any significant degree until that point.

By preference, the particle(s) is/are coated with a substance which becomes detached or separates - essentially irrespective of the concentration of the specific compound in the surrounding medium - in the period from when the composition was added to the water with which the water tank is filled, up to the point at which at least some of the water is emptied from the water tank

The basic composition is preferably in the form of a tablet.

In one embodiment proposed by the invention, the at least one particle is placed in or on the tablet in such a way that the concentration of the specific compound in the local environment of the particle or particles is high enough to prevent the coating from being dissolved to any significant degree or detached to any significant degree from the core or cores until the tablet has essentially completely dissolved.

It is particularly preferable if the particle or all the particles is or are accommodated in a cavity of the tablet, totally enclosed by the base composition.

Accordingly, the at least one cavity may contain one or more particles, in which case it alone or all together will essentially occupy the same volume as the cavity.

It is preferable if the at least one cavity has a larger volume than the particle or particles accommodated in the respective cavity.

In an alternative embodiment of the invention, the particle or particles is/are disposed loosely in the cavity.

In another alternative, the particle or particles is/are fixed in the interior of the cavity, preferably by means of an adhesive.

In another embodiment, the cavity is disposed essentially at the centre in the interior of the tablet.

It is also proposed by the invention that the tablet should have a single, substantially spherically shaped cavity.

As proposed by the invention, the cavity accommodates a single, essentially spherically shaped particle, the external diameter of which is smaller than the internal diameter of the cavity.

In another embodiment, the particle or particles is/are accommodated in at least one cavity of the tablet, which is only at least partially surrounded by the base composition.

Accordingly, it is also preferable if the cavity is provided in the form of a depression in one of the surfaces of the tablet, in which the particle or particles is/are only partially received.

In a preferred embodiment, the particle or particles is/are accommodated in the cavity or depression in such a way that it/they does/do not stand proud of (project beyond) the surface(s) of the tablet.

The invention proposes one particular embodiment, in which the cavity or the depression contains only a single particle, the volume and shape of which in the region of the cavity or



depression essentially matches the volume and shape of the cavity or depression, which is completely filled by it or them.

The cavity or depression preferably has a substantially spherically shaped cross section parallel with one of the surfaces into which it opens or in which it is disposed.

As proposed by the invention, the cavity or the depression is open at the surface(s) only to the degree that the particle or particles accommodated in it can not pass through the opening(s) of the cavity or depression.

As proposed by the invention, the particle or particles is/are preferably loosely disposed in the cavity or depression.

In an alternative, the particle or particles is/are fixed in the cavity or depression.

In one embodiment of the invention, the particle or particles is/are fixed in the cavity or depression by means of an adhesive.

In a preferred embodiment of the invention, the casing contains at least one compound which is not soluble or is only slightly soluble at the concentration of the specific compound prior to adding fresh water, but is sufficiently soluble at the concentration of the specific compound once a sufficient quantity of fresh water has been added for at least some of the material to dissolve or detach from the core(s) so that at least some of the core material is dispensed into the surrounding medium.

This being the case, it is preferable if the solubility of the compound increases as the OH ion concentration and hence the pH value in the surrounding medium decreases.

It is particularly preferable if the compound is a polymer.

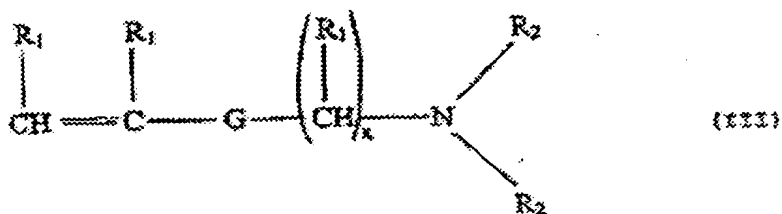
It is also preferable if the compound is a pH-sensitive polymer with at least one repeat unit with at least a basic function, which is not part of the backbone chain of the polymer.

In a preferred embodiment, the polymer has at least one repeat unit based on a compound which is selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said basic function.

The invention also proposes that the polymer should be a carbohydrate which is functionalised with said basic function.

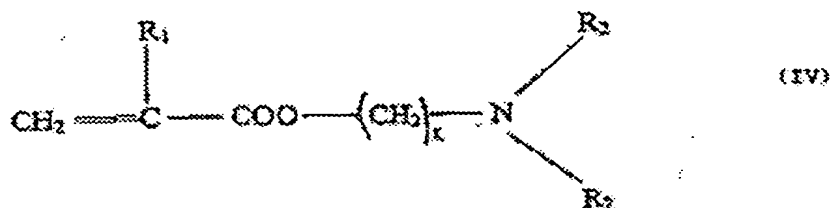
Said basic function is preferably an amine, more especially preferably a secondary or tertiary amine.

In a preferred alternative, the repeat unit is based on a compound having formula III below:



in which G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, NHCOO-, -OCONH- or -OCOO-, in which R<sub>1</sub>, independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R<sub>2</sub>, independently of one another, stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is a whole number from 1 to 6.

The repeat unit is preferably a compound having formula IV below:



in which  $\text{R}_1$ , independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms,  $\text{R}_2$ , independently of one another, stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and  $x$  is a whole number from 1 to 6.

In a preferred embodiment, the basic function is an imine or a basic aromatic group containing N, preferably a pyridine group or an imidazole group.

In another embodiment, the pH-sensitive polymer is a polymer derived from chitosan.

Finally, it is proposed by the invention that the compound should be k-carrageenan.

In one particular embodiment of the invention, the solubility of the compound increases as the concentration of  $\text{H}^+$  ions and hence the pH value in the surrounding medium decreases.

The compound is preferably a polymer.

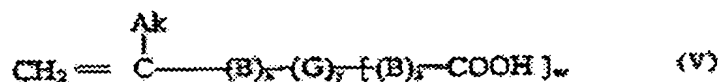
In one embodiment of the invention, the compound is a pH-sensitive polymer with at least one repeat unit based on a compound which has an acid function.

In an alternative, the polymer contains at least one repeat unit based on a compound selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said acid function.

The polymer is preferably a carbohydrate which is functionalised with said acid function.

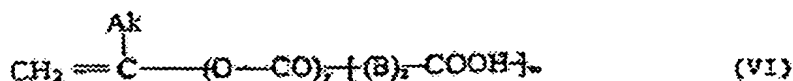
By particular preference, the acid function is a carboxyl group.

In an alternative, the repeat unit is a compound having formula V below:



in which G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, NHCOO-, -OCONH- or -OCOO-, B independently of one another, stand for a hydrocarbon group selected from straight or branched, saturated or unsaturated, optionally substituted alkylene, arylene or aralkylene, Ak stands for hydrogen or an alkyl group, preferably with 1 to 4 carbon atoms and x, y and z independently of one another are either 0 or 1 and w is a whole number from 1 to 3.

The repeat unit is preferably based on a compound having formula VI below:



in which B independently of one another, is a hydrocarbon group selected from straight or branched, saturated or unsaturated, optionally substituted alkylene, arylene or aralkylene, Ak stands for hydrogen or an alkyl group, preferably with 1 to 4 carbon atoms, y and z independently of one another are either 0 or 1 and w is a whole number from 1 to 3.

The pH-sensitive polymer is preferably derived from a polysaccharide in which some of its free hydroxyl groups are partially esterified with a polycarboxylic acid and/or some of its free hydroxyl groups are partially etherified with a product obtained by esterifying one mole of a polycarboxylic acid with one mole of a polyol.

It is also proposed by the invention that the core(s) should contain at least one material selected from the group consisting of fragrances, disinfectants and pH indicators.

It may be that the core or at least some of the cores is/are present in the form of an encapsulated liquid.

In another embodiment, the core or at least some of the cores is/are present in solid form.

The composition proposed by the invention is distinctive due to the fact that it achieves the set objective with outstanding results. The base composition in tablet format dissolves when water is added to the water reservoir and unleashes its intended effect (cleaning, removing lime, etc.). The particle or particles disposed in or on the tablet contain as the core material the sub-

stance or substances which are not intended to release their main function until at least some of the water has been drained from the water reservoir and fresh water has been added, which substances may be fragrances, disinfectants, pH indicators, etc..

This (these) substance(s) is/are protected by a covering which is stable at the concentration of a specific compound, e.g. a specific ion such as the OH ion or the H<sup>+</sup> ion (and hence a specific pH value) and optionally also the temperature of the water with which the water reservoir is initially filled and does not dissolve or become detached at all or at least not to any significant degree. Not until the concentration is significantly reduced, by draining at least some of the water from the reservoir and adding fresh water, i.e. by dilution, does the solubility of the covering become so significantly reduced that it rapidly dissolves or detaches and the actual active core material is released into the surrounding medium.

As an alternative to using the basic compound in the preferred tablet format, it would also be possible to use other dispensing formats and these are also included in the scope of the invention. For example, the particles with the covering which varies in solubility in response to a change in the concentration of the specific compound can be combined with the basic composition, i.e. encased, by a granulation or similar process. In order to ensure reduced contact between the covering and basic composition, as may be desirable in this embodiment, the particles can be encased in a further protective casing, e.g. a compound that is soluble in water irrespective of the concentration of the specific compound. With this embodiment, the basic composition and protective casing of the particles dissolve first of all during the time between the point at which the composition is added to the water tank and the point when it is at least partially drained and fresh water added, again leaving behind the particles protected with the covering proposed by the invention.

Provided that no special dispensing aids are used for dispensing purposes which might hold back the particles proposed by the invention, the particles proposed by the invention should

be large enough to ensure that they are not released to any significant degree when emptying the water tank.

The invention will now be described in more detail with reference to examples illustrated in the appended drawings. Of the drawings:

Fig. 1 is a cross section illustrating a first embodiment of the composition proposed by the invention;

Fig. 2 is a cross section illustrating a second embodiment of the composition proposed by the invention;

Fig. 3 is a cross section illustrating a third embodiment of the composition proposed by the invention;

Figs. 4a and 4b are a view in cross section and a plan view illustrating a fourth embodiment of the composition proposed by the invention; and

Fig. 5 is a cross section illustrating a fifth embodiment of the composition proposed by the invention.

Figs. 1 to Fig. 5 illustrate possible embodiments of the composition proposed by the invention. In all cases, the preferred format of a tablet is illustrated.

Fig. 1 illustrates a tablet 1, consisting of two half tablets 2 and 3, which may contain a different or the same composition.

As may be seen, a more or less semi-spherical depression 4 and 5 is provided more or less at the centre of both half tablets, which form a substantially spherical cavity when the tablet 1 is assembled.

In the embodiment illustrated here, a single particle 6 is disposed in this cavity and consists of the core 8 and the covering 9 which is sensitive to pH concentration or ion concentration, the external diameter of which is slightly smaller than the internal diameter of the cavity in the tablet. In another embodiment of the invention, however, the particle 6 may occupy the cavity completely and will sit against its walls. If the internal diameter of the cavity is slightly larger than the external diameter of the particle 6, the latter can be either loosely placed in the cavity or may be fixed by means of an adhesive placed in the gap.

The advantage gained in the embodiment in which contact between the particle and the base composition is reduced or completely prevented, is that during the manufacturing process, e.g. the consecutive steps of pressing the individual elements, any deformation and potential resultant damage to the core (cores) and/or the covering which would reduce the protective effect of the covering of the core (cores) is reliably prevented. The fact that no pressure is exerted on the particle during any phase of the production process ensures that if specific compositions are used for the core, they will not be able to "bleed" into the material of the covering and basic composition. Finally, for certain compositions of the covering 9 and/or basic composition 2, 3 it may be of advantage to avoid intimate, full-surface contact, since this could otherwise lead to undesirable reactions in the boundary layers.

In a preferred embodiment of the invention, the surface of the particle is at most in partial direct contact with the surface of the basic tablet composition surrounding it. This can be achieved by the means specifically described in this application or by any other means that will achieve the desired objective. Examples of this are arranging a smaller particle loosely in a larger cavity, fixing a smaller particle in the larger cavity such that there is little or only a



partial contact between the particle and the basic composition, applying a protective coating to the core covering proposed by the invention, etc.

By the term "local environment" used in conjunction with the particles proposed by the invention is meant the area directly surrounding said particles. The concentration of the specific compound in this local environment of the particle is the factor which determines its stability. In the preferred embodiments in tablet format, this concentration in the local environment of the particle is specifically formulated so that the tablet at least substantially totally dissolves as the molecules contained in it form a solution. Consequently, the origin of the "specific compound", at least in an initial phase following the addition of the water to the water tank, is preferably a compound which is used in the basic composition from which the tablet is made or is generated by it in the surrounding medium. In the most typical case, this will be OH ions (in the case of basic cleaning agents) or H<sup>+</sup> ions (in the case of acid lime scale removing agents), the concentration of which, in both cases, can be expressed as the pH-value.

As a means of fixing the particle in the cavity, it is obviously not only possible to use a conventional adhesive, but also other compositions and means fulfilling the same function, e.g. mechanical fixing such as an adequate friction contact between tablet and particle, at least at certain points, or a plug connection between tablet and particle. Other fixing agents may also be used between the particle and tablet in the form of compounds which optionally melt or dissolve at the temperature prevailing when water is initially added.

Naturally, a whole range of different geometric shapes may be used for the cavity in the tablet and the particle contained in it, such as ellipsoid, cylindrical, etc., for example. The shape and size of the tablet cavity and of the particle contained in it need not necessarily be the same. Accordingly, a spherical cavity might be used to accommodate a cylindrical particle, for example. All other possible combinations would also be conceivable within the scope of the present invention. The cavity could also be filled with several smaller particles instead of a single particle.

Fig. 2 illustrates a second embodiment of the composition proposed by the invention, based on a two-layer tablet 1. In this case, the top half-tablet 3 consists of two parts, which provide both an adequate cavity 5 for accommodating the particle 6 and an opening at the side 11 of the tablet. In this case, therefore, the particle 6 is not completely surrounded by the basic composition of the tablet 1 and is visible in the interior of the tablet 1 from outside. Here too, the particle may either be loosely accommodated in the cavity 5 (provided that the size of the particle 6 on the one hand and the size of the opening of the cavity 5 at the side 11 of the tablet on the other are chosen accordingly so that the particle or particles in the cavity are not able to pass through the opening) or can be fixed in the interior of the cavity 5 by appropriate means, such as an adhesive, for example.

Fig. 3 illustrates a third possible embodiment. This one is based on a tablet 1' with a uniform structure, i.e. formed by a single layer 2' of uniform composition and colour. A depression 4' is formed in said layer 2' by means of an appropriate device. The particle 6' is introduced into this depression 4' and in this case is fixed in the depression because the depression is open at the side 11' of the tablet 1' to the degree that the particle would be able to fall out of the depression if it were not fixed and it is therefore fixed by means of an adhesive 10' or by a fixing intermediate layer or by mechanical means (e.g. by friction contact). This same principle may obviously also be used for multi-layer tablets.

Here too, a whole range of different geometric embodiments are possible. For example, the depression may have a substantially circular cross-section parallel with the side 11'. However, any number of other cross-sections would also be conceivable, e.g. any polygon. As with the embodiment illustrated in Fig. 3, the particle 6' received in the depression 4' may be of any shape (regardless of the shape of the depression 4'), such as an ellipsoid, cylinder, parallelepiped, etc.

It would also be conceivable for the particle 6' to be fixed in a cavity open at both sides, for example in a cylindrical hole 4' extending through the tablet body 1', in which a matching, cylindrical particle 6' is fixed (Figs. 4a and b).

Fig. 5 illustrates another possible embodiment. This is essentially of the same structure as the embodiment illustrated in Fig. 3, i.e. a tablet 1' of uniform construction, i.e. only a single layer 2' of uniform composition and colour. In this instance, instead of a single core (as in Fig. 3), the particle 6" has a number of cores 8", all of which are embedded in a covering 9". In this embodiment it is also possible to incorporate cores of different compositions and different shapes (encapsulated material or solid cores) in one particle 6", for example.

#### Example 1

##### Preparing the core

##### a. Core for a particle enabling the controlled release of a fragrance

Oxidising cleansing agents used for sanitary purposes as additives in toilet cisterns greatly restrict the choice of fragrances which can be used in these compositions. The fact that the fragrance is not released until the cleaning agent has essentially been removed by draining the water from the cistern permits much greater flexibility in the use and development of fragrances.

For the first time, the composition proposed by the invention enables fragrances to be combined with the cleaning agent, which would otherwise be incompatible. The tablet containing the oxidising cleansing agent dissolves when placed in the cistern, which releases the particle proposed by the invention disposed on or in the tablet, the covering of which prevents the fragrance from being released and therefore attacked by the cleansing agent. When the cistern is emptied, i.e. the water mixed with the oxidising cleansing agent flows out into the toilet

bowl where it fulfils its intended function, fresh water flows in so that the dilution, i.e. the lower pH-value, "triggers" the dissolving and detachment of the particle proposed by the invention and therefore releases the core containing the fragrance, which can now fulfil its intended function in the cistern during the first outflow to the toilet bowl.

By way of example, a core of this type containing fragrance can be produced from a molten mixture of 50% molten PEG 8000, 25% fragrance and 25% diethyl phthalate, which is cooled to produce a spherical particle weighing 0.75 g, for example.

b. Core for a particle enabling the controlled release of a disinfectant

The optimum bactericidal action of a disinfectant such as benzalkonium chloride is obtained under neutral or alkaline conditions. Consequently, if benzalkonium chloride is used in acid cleansing agents (for removing lime scale) its efficiency is below the optimum.

In the case of the composition proposed by the invention, an acid cleansing tablet which is to be dispensed in a toilet cistern can be combined with a particle proposed by the invention, the core of which contains benzalkonium chloride as the disinfectant. When introduced into the cistern, the tablet dissolves releasing the particle proposed by the invention but its covering prevents the disinfectant from being released into the acid medium in question. As soon as the cistern is emptied in order to drain the acid cleaning liquor into the toilet bowl where it can fulfil its intended function, the incoming fresh water "triggers" the dissolving or detachment of the covering of the particle left behind in the cistern, so that the contents can be released from the core and can unleash their optimum action under the now neutral conditions.

A core of this type for such a particle can be produced from a molten mixture of 98% molten benzalkonium chloride and 2% blue dye, for example, which is cooled to produce a particle weighing 0.64 g, for example.

c. Preparation of a particle for releasing a pH indicator

When coffee machines are treated with an acid composition (for the purpose of removing lime scale), it is not easily possible to ascertain whether the acid used has been totally rinsed out after the treatment. Such a function could be made possible by using an acid tablet with a core containing a pH-indicator which is not released unless it is sufficiently diluted.

A core particle of this type could contain, for example, a mixture consisting of 99.7% sodium chloride and 0.3% of an appropriate indicator (e.g. methyl orange or bromocresol green).

Example 2Screening process for covering materials

As mentioned above, it is of crucial importance to the present invention that the material used for the covering of the particle core or cores containing the substance or substances which essentially do not start their function until after the water tank has been at least partially emptied and fresh water is added, has a solubility which is dependent on the concentration of a specifically selected compound. Accordingly, the covering containing a compound whose concentration is specifically formulated is essentially insoluble when exposed to the water of the water tank when the tablet has dissolved but is rendered soluble and becomes detached from the particle when the concentration drops once the water tank is at least partially drained and fresh water is added.

It has been found that the dilution resulting from at least partially draining the water containing dissolved tablet from the water tank and adding fresh water reduces the concentration 10 to 100 times, i.e. for example raises or lowers the pH-value by approximately 1 to 2 units.

On the basis of this observation, processes have been developed for screening different polymers for their suitability for use in such covering or casing materials, which involve determining the solubility of such polymers at two different concentrations, differing from one another by a factor of at least 10 and preferably 100.

The concentration values to be used during polymer screening depend on the formulation of the basic composition of the tablet in which the encased or covered particle is to be incorporated.

The value of the highest concentration used for the screening process will depend on the concentration of the selected compound encountered when the water tank is initially filled and the basic composition of the tablet has completely dissolved. Once this concentration has been determined, the lower values for the concentration should be fixed at 10 to 100 times below this higher value.

On the basis of this information, it will be within the routine capacity and knowledge of a person skilled in this field to determine the concentration values for the test solutions to be used in the testing processes described below.

#### Method of preparing the test solution and conducting and evaluating the test

The materials to be tested are dissolved in solvents in which they are readily soluble. The solutions are placed on glass plates and then dried at room temperature until they exhibit a constant weight.

The glass plates are placed in a beaker with the test solution at a controlled temperature. The solution is then stirred with a magnetic stirrer at a controlled stirring rate. After about 10 minutes, the glass plates are removed from the beaker and dried at room temperature to a constant weight. The results are expressed as a (%) weight loss.

Naturally, the screening processes must be adapted to suit the basic composition because it is this which essentially influences the concentration of the specific compound, e.g. the pH-profile, in the water tank. The objective in all cases is to check the degree of solubility of the corresponding materials in different states, namely at high or low concentration or pH-values.

Having obtained this information, it is within the routine capacity of a person skilled in this field to determine the specific test parameters for screening purposes. Two examples of screening processes are described below, which were used to test some of the materials which might be potentially used as materials for the covering of the particle proposed by the invention.

#### Screening process 1

Screening process 1A was conducted using buffer solutions as a medium for simulating an alkaline medium. Two buffer solutions were used for this purpose, prepared in the following manner:

Stock solution:	7.507 glycine buffer (Merck 104169) 5.850 g NaCl topped up with water to 1000 ml
-----------------	----------------------------------------------------------------------------------------

pH 8 buffer solution:	500 ml stock solution 500 ml distilled H <sub>2</sub> O 1.23 g 1 N NaOH
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pH 10-buffer solution:	500 ml stock solution 500 ml distilled H <sub>2</sub> O 32.6 g 1 N NaOH.
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Screening process 1B was conducted using buffer solutions as the medium for simulating an acid medium. Two buffer solutions commercially available from Merck were used for this

purpose, namely a citrate/HCl buffer solution with a pH-value of 3 and a citrate/NaOH buffer solution with a pH-value of 6.

### Screening process 2

Screening processes 2A and 2B were conducted using the following basic composition formulations in order to simulate corresponding conditions in a water tank, e.g. a toilet cistern.

The corresponding compositions were dissolved in water with 17° dH at the two different concentrations of 2 g/l and 0.02 g/l.

### Screening process 2A

#### Alkaline formulation:

<u>Substance</u>	<u>% by weight</u>
Sodium perborate monohydrate	9.00
Sodium polyphosphate	48.00
Sodium carbonate	28.00
Polyethylene glycol	4.00
Polymer	1.50
TAED	3.00
Enzymes	1.50
Surfactant	3.50
Additives	1.50
	-----
Total	100.00

### Screening process 2B

#### Acid formulation:



## BOEHMERT & BOEHMERT

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<u>Substance</u>	<u>% by weight</u>
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Amido sulphonic acid	56
Maleic acid	24
Sodium bicarbonate	20

### Screening process 3:

Screening process 3 is used to screen for compounds whose solubility changes as a function of the concentration of potassium ions. The compounds found using this screening process can be used if the concentration of potassium ions in the water tank is particularly high and is reduced accordingly by the inflow of fresh water, as described above.

Screening process 3 was conducted using the formulation below as a means of simulating the relevant conditions.

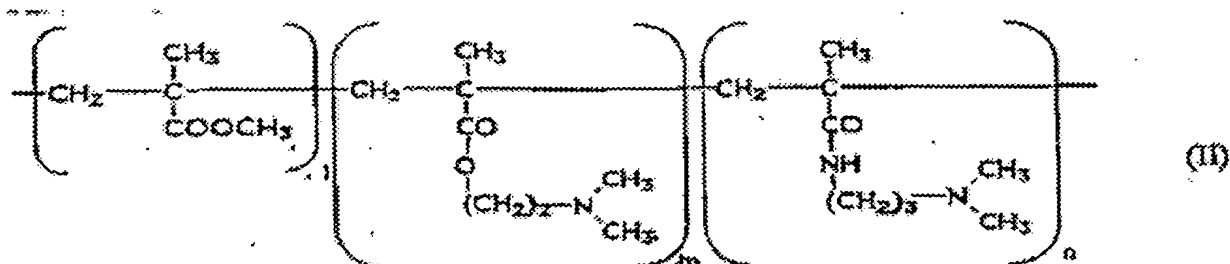
### Formulation:

Ingredient	% weight
Potassium phosphate	13.6
Potassium bicarbonate	34.00
Potassium sulphate	23.1
Potassium chloride	12.4
Potassium carbonate	9.7
Boric acid	2.0
Sodium perborate monohydrate	2.0
TAED	1.0

Paraffin	1.0
Protease	0.2

Example 3Selecting materials for covering the particles

Using the screening process described in example 2, different materials were tested for their suitability as a covering for the particles proposed by the present invention. One of these materials, hereafter referred to as "polymer 1", is a polymer as described in Japanese patent application KOKAI 61-28440, i.e. a polymer of general formula II in which  $1/(1+m+n) = 0.35$ ;  $m/(1+m+n) = 0.45$ ;  $1+m+n = 1500-1800$ .



The polymer was produced in the usual manner by bulk polymerisation. The results of screening test 1A were as follows:

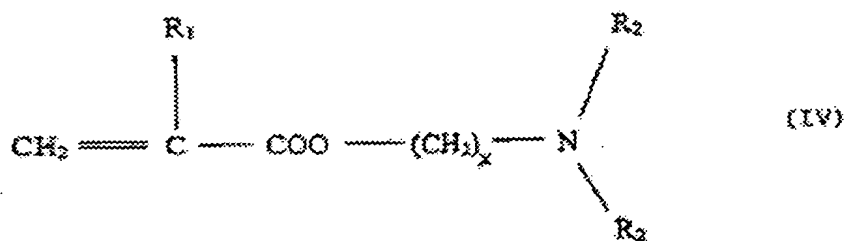
Screening test 1A:

Films of polymer 1 were made from a 10%-strength solution in isopropanol.

pH value of the buffer solution	Weight loss at 30°C [%]
10	7-8
8	81-88

Screening process 2A likewise produced good results.

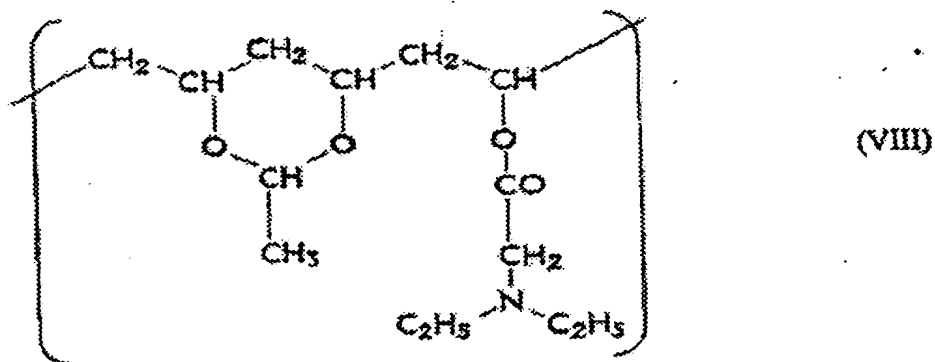
The invention is naturally not restricted to this example of a polymer and there is clearly already considerable scope for potential variations in terms of the polymers specified in Japanese patent applications KOKAI 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598 and as regards extending the range of compounds based on formula IV:



in which  $\text{R}_1$  independently of one another stand for hydrogen or an alkyl group with 1 to 3 carbon atoms,  $\text{R}_2$  independently of one another stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and  $x$  is an whole number integer from 1 to 6.

$$\begin{array}{c} R_1 \quad \cdot R_1 \\ | \quad | \\ CH = C - G - \left( \overset{\overset{R_1}{|}}{CH} \right)_x - N \begin{array}{l} \nearrow R_2 \\ \searrow R_3 \end{array} \end{array} \quad (III)$$
$$\begin{array}{c} \text{H} & & \text{O} \\ | & & || \\ \text{CH}_2=\text{C}-\text{O}-\text{C}-\text{CH}_2-\text{N} \\ & & / \quad \backslash \\ & & \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array} \quad (\text{VII})$$

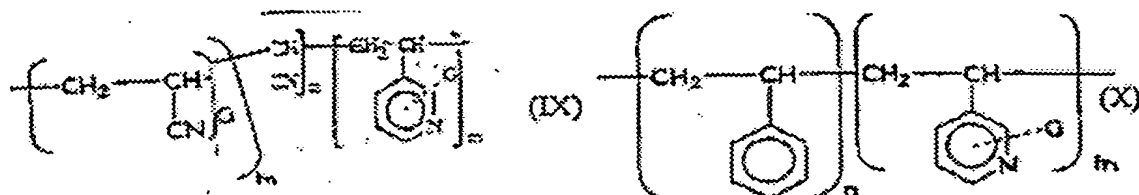
for example a pH-sensitive polymer ("polymer 2") with the repeat unit VIII, which is commercially available from the SANKYO company under the registered trade name AEA®,



Screening process 2A described above was also conducted using "polymer 2".

15 g of "polymer 2" and 5 g of Mowiol® 3-98 (Clariant) were dissolved in a mixture of water/ ethanol/ 1N HCl 12:8:1. Films were formed and tested in the manner described above. The results were comparable with those obtained for "polymer 1".

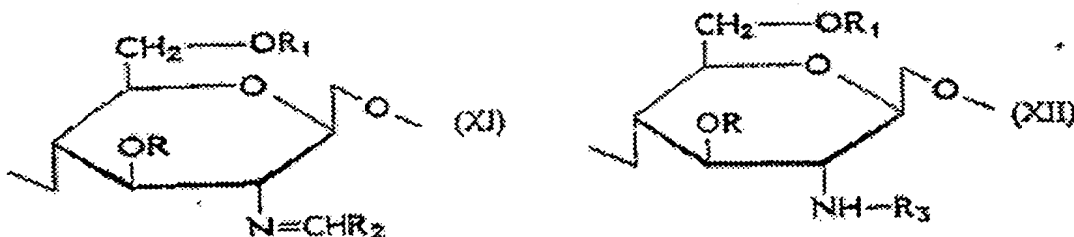
Other polymers which have the desired characteristics or which can be easily modified to render them suitable for the purposes of the present invention, are polymers of isomers or derivatives of pyridine, preferably copolymers with styrene or acrylonitrile, having formulas IX and X below, in which G is a substituent at any point on the pyridine ring.



A polymer of formula X above, namely poly(4-vinylpyridine-styrene) copolymer (Scientific Polymer Products, Inc.) "polymer 3", was tested using screening process 2A described above:

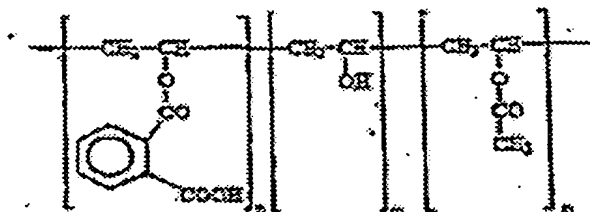
10 g of "polymer 3" were dissolved in 230 ml of water/ 1N HCl 6.25:1. Films were formed and the tests conducted as described above. The results were comparable with those obtained with "polymer 1" and "polymer 2".

Other polymers are (e.g. statistical) polymers derived from chitosan, based on the following monomer units XI and XII

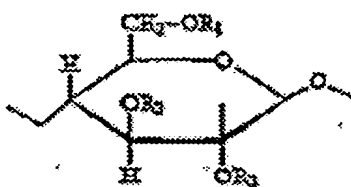


In the situation where there is a change in pH value from acid to neutral, the following examples are specific polymers which proved suitable in screening processes 1B and 2B:

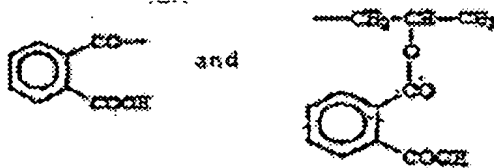
## 1. Polyvinyl acetalophthalate



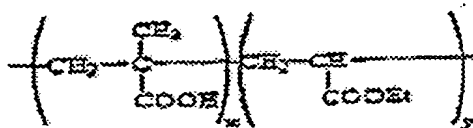
## 2. Hydroxypropyl cellulose phthalate



in which  $R_1$ ,  $R_2$  and  $R_3$  are selected, independently of one another, from the group consisting of methyl, ethyl, carboxymethyl, hydroxymethyl, acetyl



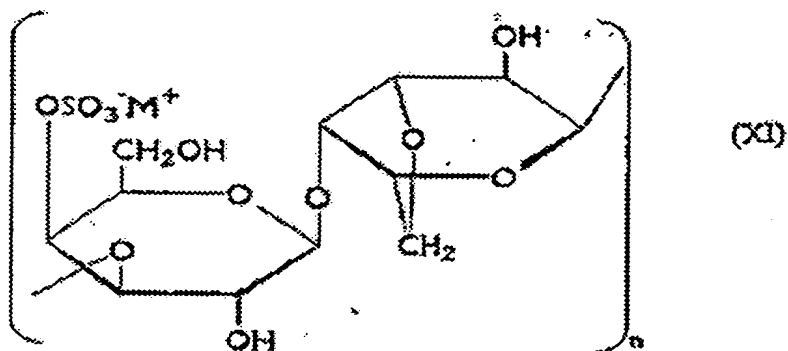
## 3. Acrylic acid/ ethyl acrylate copolymer



It would also be possible to use substances or mixtures of substances in the covering for the core material which, in terms of their solubility behaviour, react to a change in ion concentration, i.e. polymers sensitive to ion concentration. The partially hydrolysed polyvinyl acetates disclosed in patent specifications EP 0 284 191 A1 and EP 0 284 334 A2 may be considered for this purpose and are commercially available under the registered trade name Mowiol® (Clariant), which exhibit an appropriate dependence on ion concentration due to complexing of the borates with polyols. Initial tests have been successfully conducted with Mowiol® 56-88.

Another polymer that is sensitive to ion concentration is polysaccharide k-carrageenan, which was tested by screening process 3 (see example 2), which showed it to be a polymer whose solubility is dependent on the concentration of potassium ions in the surrounding medium. K-carrageenan is represented by formula XI below:





This polymer, which will be referred to as "polymer 4", was tested using screening process 3 described above.

4 g of k-carrageenan were dissolved in 96 g of water. 10 g of Mowiol® 18-88 were dissolved in 90 g of water and the two solutions mixed. The resultant solution was used to form the films and run the test, as described above. The results are set out below.

Concentration of cleansing agent	Weight loss at 30°C [%]
4 g/l	0.5-3.0
0.02 g/l	24.5-25.0

The above list of compounds suitable for the covering proposed by the invention is naturally not exhaustive. Other polymers with a solubility which changes when the concentration of a specific compound is varied, e.g. the pH value, within the desired range could be conceivably used or could be developed and are therefore also included within the scope of the present invention. Other compounds which might be considered for use as a covering proposed by the invention are those with a solubility which reacts to changes in the concentration of non-ionic compounds in the surrounding medium. Furthermore, the substances which are suitable for

use in the covering proposed by the invention are not restricted to polymeric compounds, although these are the substances described here as the preferred embodiments.

The screening processes described above or other screening methods suitable for measuring sensitivity to a concentration may be used to test other different materials, either commercially available or which can be obtained by simple modifications, for their suitability for use with the present invention. The average person skilled in this field would have no difficulty selecting these polymers by specifying an objective and applying the screening process with a view to meeting this objective accordingly.

#### Example 4

##### Preparing a particle as proposed by the invention

The different cores described in example 1 were used as a basis for manufacturing particles as proposed by the invention. These cores, individually or severally (Fig. 5), were provided with a covering by placing them in a device used to apply a film coating, of the type commonly used in the pharmaceutical industry (for example sold by the Lödige, Hüttlin, GS, Manesty and Driam companies).

In situations where the core(s) contain(s) a substance which exhibits a certain incompatibility with the material of the covering, the core can be provided with a protective coating prior to applying the covering. Various materials known from the prior art may be used for this purpose, such as cellulose, cellulose derivatives, polyvinyl alcohol, polyvinyl alcohol derivatives and mixtures thereof. If using the cores described in example 1, the protective coating used for 1a may be one which preferably contains a 10 % by weight aqueous solution of polyvinyl alcohol, respectively the polyvinyl alcohol Mowiol® 5-88 (Clariant). The quantity of coating applied may easily be varied by the skilled person depending on the composition of the core or cores and adjusted accordingly. The cores produced as described in examples 1b and 1c

were provided with the covering proposed by the invention directly, without an additional protective coating.

The covering may essentially be applied to the core or cores or on top of the protective coating in any quantity and thickness, provided care is taken to ensure that the covering will dissolve or detach sufficiently well on exposure to added fresh water that the substance contained in the core or cores is able to unleash its effect. In a preferred embodiment, the concentration-sensitive covering material is applied to the core in a quantity of 1 - 10 % by weight, preferably 4 - 8 % by weight, by reference to the weight of the particle as a whole.

#### Example 5

##### Preparation of tablets as proposed by the invention

###### a. Preparation of a tablet for use in a coffee machine

A 2-layer tablet suitable for accommodating a covered particle proposed by the invention and of the type described in examples 1c and 4 in a cavity provided in the tablet can be made by compressing the powdered ingredients in machines that are essentially known from the prior art using standard operating parameters. One possible format for such a tablet is a square-shaped tablet comprising two layers essentially of identical thickness, the largest surface of these layers incorporating a semi-spherical depression so that the two halves form a substantially spherical cavity in the interior when the two half-tablets are assembled (see Fig. 1).

The composition of the tablet is set out in Table 2 below, the two half tablets being made from the same composition, which is pressed under a pressure of approximately 900 kg/cm<sup>2</sup>.

Table 2

Ingredient	% by weight
Amido sulphonic acid	56
Maleic acid	24
Sodium bicarbonate	20

The total weight of both half-tablets is 20 g, for example. The cavity formed when the half-tablets are assembled should have an internal diameter that is larger than the external diameter of the particle proposed by the invention.

The particle prepared as described in examples 1c and 4 is placed in the semi-spherical depression of one of the two half-tablets. A fixing substance such as an adhesive (e.g. polyethylene glycol, polyvinyl ether, polyvinyl alcohol, silicate, preferably molten PEG 4000) is then applied to the corresponding surface of the half-tablet and the second half-tablet is pressed onto the first half-tablet.

b. Preparation of a tablet for use in a toilet cistern

A 2-layer tablet capable of accommodating a covered particle as proposed by the invention and described in examples 1a and 4 in a cavity in the tablet can be made by pressing the powdered ingredients in essentially the same way as described in example 5a.

The composition of the tablet is set out in Table 3 below and the two half-tablets made from the same composition are pressed under a pressure of approximately 800 kg/cm<sup>2</sup>

Table 3

Ingredient	% weight
Sodium tripolyphosphate	20.0
Sodium carbonate	10.0
Sodium bicarbonate	20.0
Trisodium-NTA	8.0
Sodium metasilicate	20.0
Sodium sulphate	8.0
Sodium dichloro-isocyanurate	8.0
Polymer	1.5
Non-ionic surfactant	4.5

The total weight of the two half-tablets is 23 g, for example.

c. Preparation of a tablet for use in a toilet cistern

A 2-layer tablet capable of accommodating a covered particle as proposed by the invention and described in examples 1a and 4 in a cavity in the tablet can be made by pressing the powdered ingredients in essentially the same way as described in example 5a.

The composition of the tablet is set out in Table 4.

Table 4

Ingredient	% weight
Potassium phosphate	13.6
Potassium bicarbonate	34.00
Potassium sulphate	23.1
Potassium chloride	12.4
Potassium carbonate	9.7
Boric acid	2.0
Sodium perborate monohydrate	2.0
TAED	1.0
Paraffin	1.0
Protease	0.2

d. Preparing a tablet for use in a toilet cistern

A 2-layer tablet capable of accommodating a covered particle as proposed by the invention and described in examples 1a and 4 in a cavity in the tablet can be made by pressing the powdered ingredients in essentially the same way as described in example 5a.

The composition of the tablet is set out in Table 5 below and the two half-tablets are of the same composition and pressed at a pressure of approximately 900 kg/cm<sup>2</sup>.

Table 5

Ingredient	% by weight
Amido sulphonic acid	56
Maleic acid	24
Sodium bicarbonate	20

The total weight of the two half-tablets together is 20 g, for example.

The characterising features of the invention disclosed in the description, claims and drawings may essentially be used individually and in any combination to implement the different embodiments of the invention.

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## ANWALTSSOZIOZETÄT

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Bremen,

New application  
(Patent)

**BK3669**

28 July 1998

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"Composition for use in a water reservoir "

### Claims

1. Composition for use in a water reservoir in the kitchen or bathroom environment, characterised by
  - a basic composition (2, 3; 2') which starts to function essentially when the water reservoir is first filled with water; and
  - at least one particle (6; 6'; 6'') with



- at least one core (8; 8'; 8'') containing at least one substance, which starts to function essentially after at least some of the water from the first filling process has been emptied from the water reservoir and fresh water is added; and
- a covering (9; 9'; 9'') substantially completely surrounding the core or cores and containing at least one compound, the solubility of which increases as the concentration of a specific compound in the surrounding medium decreases;

means being provided so that the covering (9; 9'; 9'') of the core (8; 8') or cores (8'') is essentially prevented from significantly dissolving or becoming substantially detached until there is an inflow of fresh water to the water reservoir.

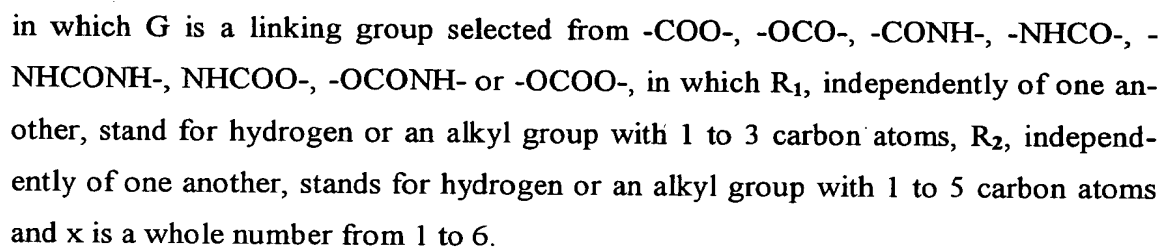
2. Composition as claimed in claim 1, characterised in that the concentration of the specific compound in the local environment of the particle or particles (6; 6'; 6''), up until the inflow of fresh water to the water reservoir, is high enough to prevent the covering (9; 9'; 9'') from dissolving or becoming detached to any significant degree until that point.
3. Composition as claimed in claim 2, characterised in that the particle(s) (6; 6'; 6'') is/are coated with a substance which becomes detached or separates - essentially irrespective of the concentration of the specific compound in the surrounding medium - during the period starting from when the composition was added to the water with which the water reservoir is filled, up to the point at which at least some of the water is emptied from the water reservoir.
4. Composition as claimed in one of claims 1 to 3, characterised in that the basic composition is in the form of a tablet (1; 1').

5. Composition as claimed in claim 4, characterised in that at least one particle (6; 6'; 6'') is placed in or on the tablet (1; 1') in such a way that the concentration of the specific compound in the local area around the particle or particles is high enough to prevent the covering from being dissolved to any significant degree or detached to any significant degree from the core or cores until the tablet (1; 1') has essentially completely dissolved.
6. Composition as claimed in claim 5, characterised in that the particle or all the particles (6) is or are accommodated in a cavity (4, 5) of the tablet (1), totally enclosed by the base composition (2, 3).
7. Composition as claimed in claim 6, characterised in that the at least one cavity (4, 5) may contain one or more particles (6), in which case it alone or all together will essentially occupy the same volume as the cavity (4, 5).
8. Composition as claimed in claim 6, characterised in that the at least one cavity has a larger volume than the particle or particles (6) accommodated in the respective cavity (4, 5).
9. Composition as claimed in claim 8, characterised in that the particle or particles (6) is/are disposed loosely (4, 5) in the cavity.
10. Composition as claimed in claim 8, characterised in that the particle or particles (6) is/are fixed in the interior of the cavity (4, 5).
11. Composition as claimed in claim 10, characterised in that the particle or particles (6) is/ are fixed in the interior of the cavity (4, 5) by means of an adhesive.

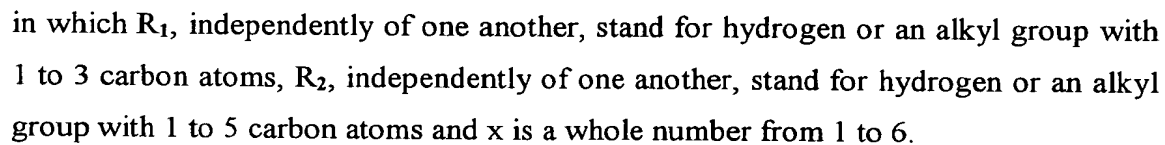
12. Composition as claimed in claim 10, characterised in that the cavity (4, 5) is disposed essentially at the centre in the interior of the tablet (1).
13. Composition as claimed in one of claims 6 to 12, characterised in that the tablet (1) has a single, substantially spherically shaped cavity (4, 5).
14. Composition as claimed in one of claims 8 to 13, characterised in that the cavity (4, 5) accommodates a single, essentially spherically shaped particle (6), the external diameter of which is smaller than the internal diameter of the cavity.
15. Composition as claimed in claim 5, characterised in that the particle or particles (6'; 6'') is/are accommodated in at least one cavity (4') of the tablet (1'), which is only at least partially surrounded by the base composition (2').
16. Composition as claimed in claim 15, characterised in that the cavity is a depression (4') in one of the surfaces (11') of the tablet (1'), in which the particle or particles (6'; 6'') is/are at least partially received.
17. Composition as claimed in claim 15 or 16, characterised in that the particle or particles (6'; 6'') is/are accommodated in the cavity or depression (4') in such a way that it/they do/does not stand proud of (project beyond) the surface(s) (11') of the tablet (1').
18. Composition as claimed in claim 15 to 17, characterised in that the cavity or the depression (4') contains only a single particle (6'; 6'') , the volume and shape of which in the region of the cavity or depression essentially matches the volume and shape of the cavity or depression (4') and essentially completely fills it or them.

19. Composition as claimed in one of claims 15 to 18, characterised in that the cavity or depression (4') has a substantially spherically shaped cross section parallel with one of the surfaces (11') into which it opens or in which it is disposed.
20. Composition as claimed in one of claims 15 to 19, characterised in that the cavity or the depression (4') is open at the surface(s) (11) only to the degree that the particle or particles (6'; 6'') accommodated in it can not pass through the opening(s) of the cavity or depression (4').
21. Composition as claimed in claim 20, characterised in that the particle or particles (6'; 6'') is/are preferably loosely disposed in the cavity or depression (4').
22. Composition as claimed in one of claims 15 to 20, characterised in that the particle or particles (6'; 6'') is/are fixed in the cavity or depression (4').
23. Composition as claimed in claim 22, characterised in that the particle or particles (6'; 6'') is/are fixed in the cavity or depression (4') by means of an adhesive (10').
24. Composition as claimed in one of the preceding claims, characterised in that the covering (9; 9'; 9'') contains at least one compound which is not soluble or is only slightly soluble at the concentration of the specific compound prior to adding fresh water, but is sufficiently soluble at the concentration of the specific compound once a sufficient quantity of fresh water has been added for at least some of the material to dissolve or detach from the core(s) so that at least some of the core material is dispensed into the surrounding medium.
25. Composition as claimed in claim 24, characterised in that the solubility of the compound increases as the OH ion concentration and hence the pH value in the surrounding medium decreases.

26. Composition as claimed in claim 25, characterised in that the compound is a polymer.
27. Composition as claimed in claim 26, characterised in that the compound is a pH-sensitive polymer with at least one repeat unit with at least a basic function, which is not part of the backbone chain of the polymer.
28. Composition as claimed in claim 27, characterised in that the polymer has at least one repeat unit based on a compound which is selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said basic function.
29. Composition as claimed in claim 27, characterised in that the polymer is a carbohydrate which is functionalised with said basic function.
30. Composition as claimed in one of claims 27 to 29, characterised in that the basic function is preferably an amine.
31. Composition as claimed in claim 30, characterised in that the basic function is a secondary or tertiary amine.
32. Composition as claimed in claim 31, characterised in that the repeat unit is based on a compound having formula III below:



33. Composition as claimed in claim 32, characterised in that the repeat unit is a compound having formula IV below:



34. Composition as claimed in one of claims 27 to 29, characterised in that the basic function is an imine.
35. Composition as claimed in one of claims 27 to 29, characterised in that the basic function is a basic aromatic group containing N.
36. Composition as claimed in claim 35, characterised in that the basic function is a pyridine group.
37. Composition as claimed in claim 35, characterised in that the basic function is an imidazole group.
38. Composition as claimed in claim 29, characterised in that the pH-sensitive polymer is a polymer derived from chitosan.
39. Composition as claimed in claim 24, characterised in that the compound is k-carrageenan.
40. Composition as claimed in claim 24, characterised in that the solubility of the compound increases as the concentration of  $H^+$  ions and hence the pH value in the surrounding medium decreases.
41. Composition as claimed in claim 40, characterised in that the compound is a polymer.
42. Composition as claimed in claim 41, characterised in that the compound is a pH-sensitive polymer with at least one repeat unit based on a compound which has an acid function.

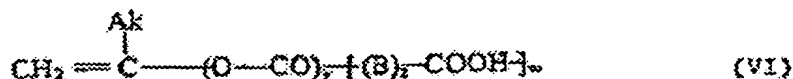
43. Composition as claimed in claim 42, characterised in that the polymer contains at least one repeat unit based on a compound selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said acid function.
44. Composition as claimed in claim 42, characterised in that the polymer is a carbohydrate which is functionalised with said acid function.
45. Composition as claimed in one of claims 42 to 44, characterised in that the acid function is a carboxyl group.
46. Composition as claimed in claim 45, characterised in that the repeat unit is a compound having formula V below:



in which G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, NHCOO-, -OCONH- or -OCOO-, B independently of one another, stand for a hydrocarbon group selected from straight or branched, saturated or unsaturated, optionally substituted alkylene, arylene or aralkylene, Ak stands for hydrogen or an alkyl group, preferably with 1 to 4 carbon atoms and x, y and z independently of one another are either 0 or 1 and w is a whole number from 1 to 3.

47. Composition as claimed in claim 46, characterised in that the repeat unit is based on a compound having formula VI below:





in which B, independently of one another, stand for a hydrocarbon group selected from straight or branched, saturated or unsaturated, optionally substituted alkylene, arylene or aralkylene, Ak stands for hydrogen or an alkyl group, preferably with 1 to 4 carbon atoms, y and z independently of one another are either 0 or 1 and w is a whole number from 1 to 3.

48. Composition as claimed in claim 44, characterised in that the pH-sensitive polymer is derived from a polysaccharide in which some of its free hydroxyl groups are partially esterified with a polycarboxylic acid and/or some of its free hydroxyl groups are partially etherified with a product obtained by esterifying one mole of a polycarboxylic acid with one mole of a polyol.
49. Composition as claimed in one of the preceding claims, characterised in that the core(s) (8; 8'; 8'') contain(s) at least one material selected from the group consisting of fragrances, disinfectants and pH indicators.
50. Composition as claimed in claim 49, characterised in that the core (8; 8') or at least some of the cores (8'') is/are present in the form of an encapsulated liquid.
51. Composition as claimed in claim 49 or 59, characterised in that the core (8; 8') or at least some of the cores (8'') is/are present in solid form.

Abstract

Composition for use in a water reservoir in the kitchen or bathroom environment, characterised by a basic composition which starts to function essentially when the water reservoir is first filled with water; and at least one particle with at least one core containing at least one substance which starts to function essentially after at least some of the water from the first filling process has been emptied from the water reservoir and fresh water is added, and a covering essentially totally surrounding the core(s) and containing at least one compound, the solubility of which increases as the concentration of a specific compound in the surrounding medium decreases; means being provided so that the covering of the core or cores is essentially prevented from significantly dissolving or becoming substantially detached until there is an inflow of fresh water to the water reservoir.